



Ozone treatment of soil contaminated with aniline and trifluralin [☆]

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Abstract

Column studies were conducted to determine the ability of ozone to degrade aniline and trifluralin in soil. Ozone rapidly degraded aniline from soil under moist soil conditions, 5% (wt). Removal of 77–98% of [UL-¹⁴C]-aniline was observed from soil columns (15 ml, i.d. = 2.5 cm), exposed to 0.6% O₃ (wt) at 200 ml/min after 4 min. Initial ozonation products included nitrosobenzene and nitrobenzene, while further oxidation led to CO₂. Ring-labeled-[UL-¹⁴C]-trifluralin removal rates were slower, requiring 30 min to achieve removals of 70–97%. Oxidation and cleavage of the *N*-propyl groups of trifluralin was observed, affording 2,6-dinitro-4-(trifluoromethyl)-aniline, 2,6-dinitro-*N*-propyl-4-(trifluoromethyl)-benzamine, and 2,6-dinitro-*N*-propyl-*N*-acetyl-4-(trifluoromethyl)-benzamine. Base solutions revealed that trifluralin was similarly oxidized to CO₂, where 72–83% of the activity recovered comprised ¹⁴CO₂. Use of ozone-rich water improved contaminant removal in trifluralin-amended soil columns, but did not improve removal in aniline, pentachloroaniline, hexachlorobenzene amended soil columns, suggesting that ozonated water may improve contaminant removal for reactive contaminants of low solubility.

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1. Introduction

Soil and groundwater contamination from pesticides has become an issue of interest as incidents of contamination have been documented around the world (Boesten and Van der Linden, 1991; Byrne, 1991; Mass et al., 1995; Balinova and Mondesky, 1999; Close and Rosen,

2001). Efforts to find effective methods to treat soil and water contaminated with pesticides and other compounds have led to the study of alternative remediation strategies (Tyre et al., 1991; Rajput et al., 1994; McFarland, 1996; Amarante, 2000). The introduction of ozone may provide an effective method for treatment soils contaminated with pesticides. Ozone can be readily transported through columns packed with a number of geological materials, including Ottawa sand, Jumunjin sand, Metea soil, Borden aquifer material, and Wurthsmith aquifer material (Masten and Davies, 1997; Choi et al., 2000). Ozone has also been shown to degrade hydrocarbons, polyaromatic hydrocarbons, and volatile organic compounds in soils (Yao and Masten, 1991; Hsu et al., 1993; Nelson and Brown, 1994; Masten and Davies, 1997; Eberius et al., 1997). In situ studies and

[☆] Mention of specific products or supplier is for identification and does not imply endorsement by US Department of Agriculture to the exclusion of other suitable products or suppliers.

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transport models have demonstrated that ozone can be effectively transported through soil (Clayton, 1998; Hsu and Masten, 2001).

Ozone is a strong oxidant ($E^0 = 2.07$ V) and will rapidly oxidize a number of pesticides in aqueous systems (Reynolds et al., 1989; Somich et al., 1990; Beltran et al., 1993). This study focuses on the use of ozone to treat soils contaminated with trifluralin. Trifluralin belongs to a class of dinitroanilines possessing herbicidal properties. Concern over trifluralin contamination stems from its known human carcinogen and that current methods of remediation are limited (McFarland et al., 1996). Aniline, pentachloroaniline, and hexachlorobenzene were also studied. Aniline was selected because of its importance in pesticide manufacturing and waste as it is the terminus for trifluralin and a variety of agricultural chemicals, including formamidines, carbanilates, and phenylureas. Pentachloroaniline and hexachlorobenzene were used to study the influence of soil organic matter on ozone treatment.

Ozone application to contaminated soils has several potential benefits. Ozone can rapidly oxidize many highly toxic contaminants to easily biodegradable and non-toxic compounds which are often more hydrophilic (Glaze, 1986; Heinze et al., 1992; Sarasa et al., 1998; Nam and Kukor, 2000). Further, ozonation has been shown to increase the low molecular acid fraction and the hydrophilic nature of soil organic matter (Ohlenbusch et al., 1998). The fact that ozone can increase aqueous solubility suggests that it can be used to enhance the desorption of contaminants from soil, potentially improving biodegradation or removal via soil washing processes. However, the effectiveness of ozone may be limited by factors such as competing reactions with soil organic matter and soil conditions, porosity and pH.

This study was conducted to determine the usefulness of ozone in the direct remediation of contaminated soil. The objectives of this study were to, (1) examine the rates of degradation for trifluralin and aniline in moist soil columns exposed to ozone gas, and (2) examine the effect of ozonated water on contaminant removal and mobility under saturated conditions.

2. Materials and methods

2.1. Materials

Analytical grade aniline, pentachloroaniline, hexachlorobenzene (purities 99%) and trifluralin (purity 98%), and [Ring-UL- 14 C] labeled aniline and trifluralin were obtained from Sigma Chemical Co. Lignin (organosolv) was obtained from Aldrich and was used as a supplemental organic matter source for the column

Table 1
Selected soil properties of Evesboro sand and Christiana sandy loam

	Evesboro C1	Evesboro B2	Christiana Ap
<i>Soil texture^a</i>			
Sand (%)	95	89	15
Silt (%)	3	8	53
Clay (%)	2	3	32
Total carbon (%) ^b	0.03	0.12	0.77
Soil pH ^c	5.5	5.3	4.7

^a Johnson and Chu (1983).

^b Determined on dried soil samples using a Shimadzu TOC5000, total organic carbon analyzer.

^c Determined by glass electrode method (Van Lagen, 1996).

studies. The elemental analysis for the lignin provided by the manufacturer was 65.7% C, 5.5% H, 0.1% N, 28.7% O, and 0.0% ash, with a surface area of 1.8 m²/g.

Stock solutions of aniline and trifluralin were prepared by dissolving ≈ 0.5 g of analytical grade aniline or trifluralin and 0.2 μ Ci of the respective radiolabeled material in 25 ml of methanol. Stock solutions of pentachloroaniline and hexachlorobenzene were prepared by dissolving 0.5 g of pentachloroaniline or hexachlorobenzene in 25 ml of methanol. The soils used in this study were an Evesboro sand and a Christiana sandy loam (Table 1). The Evesboro series consists of deep, well drained soils formed in regolith of unconsolidated, sandy sediments and is taxonomically a fine-loamy, siliceous, semiactive, mesic Typic Hapludults (Soil Survey Division, 2002). The Christiana series consists of very deep, well drained soils with slow to moderately slow permeability on uplands and sideslopes of the dissected Coastal Plain. The Christiana soil series is taxonomically a fine, kaolinitic, mesic Typic Paleudults (Soil Survey Division, 2002). Ozone gas was generated using a PCI ozone generator model GL-1B (PCI Ozone Corporation, West Caldwell, NJ 07006) with dry oxygen feed (dew point ≈ -70 °C). To maintain soil moisture levels for column ozonation studies on unsaturated columns, ozone gas was humidified by passing the gas stream through an impinger containing 50 ml of deionized water. Ozone concentrations were determined through titration of acidified KI solutions using standardized 0.01 N Na₂S₂O₃ (Flamm, 1977).

2.2. Preparation of soil columns

Soil column studies were performed to examine the effect of ozone gas on aniline and trifluralin under unsaturated soil conditions, and to determine the effect of ozone-rich water on the removal of aniline, trifluralin, pentachloroaniline, and hexachlorobenzene from soil

columns. Soils were air dried and sifted through a no. 16 mesh screen (US Standard). One-hundred and ten grams of sifted soil was amended with 1 ml aliquots of stock solutions of aniline, trifluralin, pentachloroaniline, or hexachlorobenzene.

For unsaturated soil columns, the soils were also amended with 5 ml of deionized water to establish residual moisture content and hand-mixed again. Moisture content was verified gravimetrically before and after gas treatment. Approximately 15 g of amended, moist soil were added to a series of 7 pyrex columns (12×2.5 cm). The inlet for each column was made of stainless steel and the outlet of Teflon.

For saturated columns studies, 25 g of amended soil was added to each of a series of 4–60 ml polypropylene syringes fitted with glass fiber filters to prevent the elution of soil fines.

2.3. Ozonation procedures and apparatus

For ozonation of unsaturated soil columns, humidified ozone gas was supplied to the soil columns at 0.6% O_3 (wt) and 0.2 l/min for 0.5, 1, 2, 3, and 4 min. Trifluralin amended columns were exposed to ozone for longer times, up to 30 min, to achieve comparable removals. Ozone-free oxygen at 0.2 l/min was supplied to a sixth column to determine loss due to direct volatilization. The seventh column, which was not exposed to the gas streams, was used as a control. As shown in Fig. 1a, the outlet ozone gas stream was bubbled sequentially through three 60 ml impingers. The first impinger was filled with a phosphate buffered 1% KI solution to determine ozone concentration in the outlet gas stream, and the final two impingers were filled with a 1 N KOH solution to trap $^{14}CO_2$. The solutions were collected, sampled, and replaced following each time interval. For columns exposed to ozone-free oxygen, the outlet gas stream was bubbled directly to an impinger containing 60 ml of methanol.

Gas flow rates were controlled using two parallel mass flow controllers (Model UFC-1500, Unit Instruments, Orange, CA). While gas (0.2 l/min) from the first mass flow controller outlet was directed to the column inlet, the gas from the second mass flow controller was directed to the ozone monitor. The ozone gas inlet concentrations were also verified prior to each study by bubbling the inlet gas stream through 60 ml of phosphate buffered 1% KI solution for 30 s.

Studies were also performed to determine ozone consumption rates for contaminant-free soils. This was accomplished by passing ozone gas at 0.6% O_3 and 0.2 l/min through columns containing 5 g of soil. The soils, which were amended with 5 ml of deionized water, were exposed to humidified ozone gas. Ozone concentrations in the column outlet gas streams were determined by UV

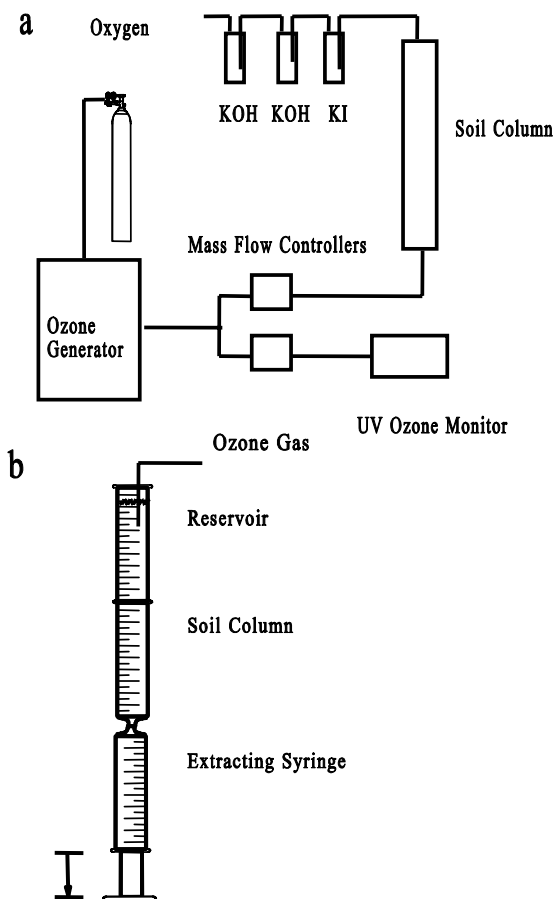


Fig. 1. Experimental apparatus for soil ozonation: (a) ozone generation, (b) experimental design for soil column experiments.

spectrophotometry, and by bubbling the gas stream through 60 ml of 1% KI solution. Total ozone consumption was determined from the difference between inlet and outlet ozone concentrations. The ozone consumption experiment was performed several times for each soil.

Saturated column studies were performed by vacuum extraction using the 60 ml polypropylene syringes (Fig. 1b), with a mechanical vacuum extractor (Centurion International, Inc.). Extractant was drawn from the syringe reservoirs, through column syringes at 1.8 ml/min and collected in the lower syringe for sampling. Each column study was performed at least three times.

Two sets of two columns were used for the saturated column studies. Reservoirs were filled with either ozone-free, deionized, organic-free water, or ozone-rich, deionized, organic-free water. Ozone concentrations were maintained in the ozone-rich reservoirs at 3.5 mg/l by supplying gas continuously to reservoirs at 0.5 l/min. The influence of pH on contaminant removal was

studied by treating Evesboro C soil with trifluralin or aniline as described earlier, adding 25 g of amended soil to syringe columns, and passing through them solutions of ozone rich, 3.5 mg/l, organic-free water buffered at pH 4, 7, and 12. The influence of organic matter was studied by adding lignin to Evesboro C soil at 0.07 and 0.15% organic carbon. Adsorption of the lignin to the soil was verified by vacuum extraction of soil samples and organic carbon analysis of soil and extraction volumes. Soil/lignin mixtures were then amended with trifluralin or aniline as described earlier, and 25 g of amended soil added to each of the syringe columns. Ozone-free or ozone-rich, 3.5 mg/l, deionized organic free water was passed through the columns.

Experiments were conducted to determine the effect of ozone-rich water on soil organic matter, using uncontaminated soil. Solutions from columns treated with ozone-rich water and ozone-free water were analyzed for dissolved organic carbon (DOC) using a Shimadzu, TOC5000, Total Organic Carbon Analyzer.

2.4. Analytical methods

2.4.1. Ozone-gas soil columns studies

To determine contaminant concentrations and activities present on unsaturated soil columns, the contents of each soil column were emptied into 50 ml beakers. The soils were well mixed, and samples, ≈ 1 g each, were weighed and transferred to 10 ml glass tubes. Each soil sample was extracted three times with 10 ml of methanol by adding methanol to the glass tubes, shaking using a vortex shaker for 2 min, and filtering the supernatant by vacuum through a 1 μ m glassfiber filter. Activities were determined by liquid scintillation counting (Beckman LS6000IC, Beckman Instruments, Fullerton, CA) of 5 ml samples. Contaminant concentrations were determined by high pressure liquid chromatography (HPLC) (see below). Activity and contaminant extraction efficiencies were determined (Table 2). Separate soil samples were also collected periodically and extracted with ethyl acetate for qualitative analysis by gas chromatography/mass spectroscopy (GC/MS).

The presence of $^{14}\text{CO}_2$ in the KOH traps was determined by combining 2 ml of trapping solution with

2 ml of saturated BaCl_2 solution, centrifuging, and measuring the supernatant for radioactivity. Activities in methanol solutions were also determined by liquid scintillation counting of 5 ml samples of the solutions.

2.4.2. Ozone-rich water soil columns studies

Samples (5 ml) of the ozonated reservoirs were collected to determine ozone concentration. The samples were immediately added to buffered, pH 6.5, 1% KI solutions, and analyzed by iodometric titration. For comparison, additional samples were collected and added to solutions of potassium indigo trisulfonate, and analyzed using spectrophotometric methods (Bader and Hoigne, 1982). Ozone concentrations in extracted volumes were determined by adding 5 ml of KI solution to lower syringes. Extractant volumes were collected and analyzed by iodometric titration. Activities in extracted volumes from lower syringes were determined by liquid scintillation counting of 5 ml samples.

2.4.3. Aniline, trifluralin, pentachloroaniline, and hexachlorobenzene

Organic contaminant concentrations were determined by HPLC (Waters (Milford, MA) Model 616 LC and Millennium[®] system equipped with two 510 pumps, a Model 717 autosampler, and a Model 996 photodiode array detector). Separations were achieved for aniline using isocratic flow: 26% acetonitrile in water at a flow rate of 1.25 ml/min on a Beckman (Fullerton, CA) C-18 (ODS 5 μ m), end-capped, 4.6 mm \times 25 cm steel-jacketed column. Peak identification was established by comparison of the retention times and UV spectra with a standard. Separations were achieved for trifluralin, pentachloroaniline, and hexachlorobenzene using the same columns, but with an isocratic flow of 75% acetonitrile in water.

For ozonation product identification, ethylacetate-extracted samples were analyzed using a Hewlett-Packard 5890 gas chromatograph attached to a Hewlett-Packard 5989A mass spectrometer. Gas chromatographic conditions for trifluralin products were as follows: 30 m DB-5MS (J&W) capillary column, i.d. 0.2 mm and 0.33 μ m film thickness; splitless injection with 0.5 min purge off time; column head pressure 0.12 MPa injector temperature 25 $^\circ\text{C}$; temperature program, initial temperature 90 $^\circ\text{C}$, hold for 1 min, 8 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$, hold for 5 min; GC/MS interface temperature 27 $^\circ\text{C}$. The mass spectrometry was obtained in the negative chemical ionization mode with quadrupole temperatures of 150 and 100 $^\circ\text{C}$, respectively. Aniline products were analyzed in electron impact mode, with an initial column temperature of 50 $^\circ\text{C}$, held for 2 min and raised to 170 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$.

Table 2
Soil contaminant and activity extraction efficiency presented as % of applied

Soil	Aniline (parent/activity)	Trifluralin (parent/activity)
Evesboro C1	87 \pm 6/85 \pm 5	96 \pm 4/97 \pm 3
Evesboro B2	85 \pm 3/84 \pm 2	94 \pm 3/99 \pm 3
Christiana Ap	77 \pm 2/72 \pm 4	91 \pm 2/101 \pm 4

3. Results and discussion

3.1. Ozone consumption and breakthrough

Fig. 2 shows ozone breakthrough curves for the three uncontaminated soils. Ozone demands of 0.026 and 0.051 mg/g soil were observed for Evesboro C1 and B2 soils respectively, while the ozone demand for the Christiana soil was of 1.82 mg/g. These results are comparable to ozone breakthrough studies conducted by Masten and Davies (1997) on Ottawa sand and Metea subsoil. Ozone rapidly passed through Evesboro soil columns, but was readily consumed by Christiana soil during the first 5 min of treatment. Soil properties suggest that this is the result of ozone consumption by soil organic matter. However, the relationship between ozone consumption and organic carbon content was not linear, suggesting that other factors, such as soil surface area, are also important. For example, the Christiana soil has a clay and silt content significantly higher than the Evesboro soils. After screening and amendment, the Christiana soil was found to possess a significantly finer texture than the Evesboro soils, indicating a higher surface area. This high surface allows more contact area for the ozone to react, thereby decomposing the ozone more rapidly from the gas stream.

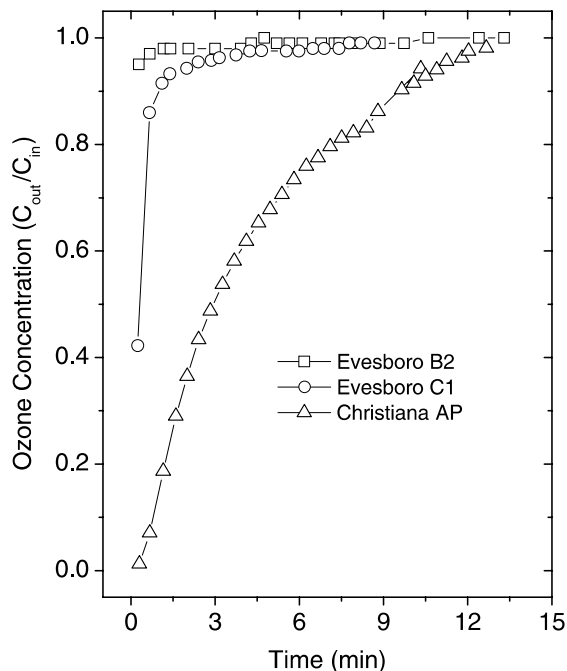


Fig. 2. Ozone gas breakthrough curves for soil columns.

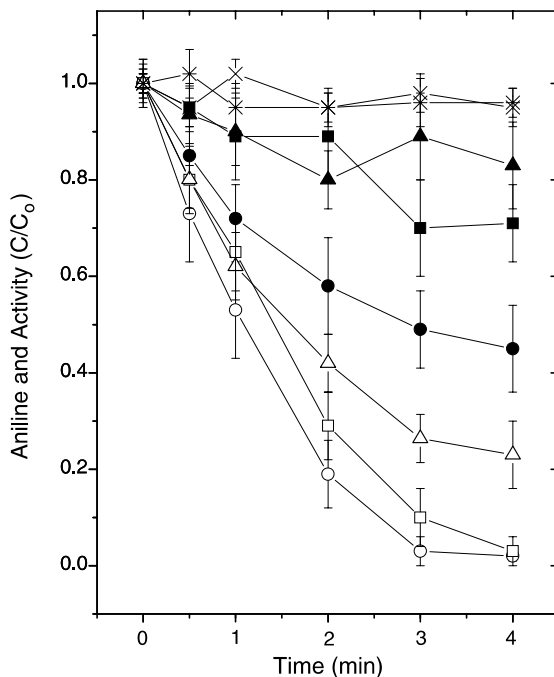


Fig. 3. Treatment of aniline in soil columns using ozone gas: (○) parent compound remaining in Evesboro C1 soil columns; (●) ¹⁴C remaining in Evesboro C1 soil columns; (□) parent compound remaining in Evesboro B2 soil columns; (■) ¹⁴C remaining in Evesboro B2 soil columns; (△) parent compound remaining in Christiana soil columns; (▲) ¹⁴C remaining in Evesboro B2 soil columns. (×) and (*) represent the parent and ¹⁴C remaining using ozone-free oxygen.

3.2. Contaminant degradation

The disappearance of aniline from soil columns exposed to ozone gas is shown in Fig. 3. Aniline concentration decreased rapidly in Evesboro soil columns, with less than 3% remaining after 4 min of exposure. Approximately 23% of aniline remained in Christiana soil columns after the same time period. A portion of the aniline loss can be attributed to volatilization, because aniline concentrations and activities decreased by 11–26% in columns exposed to ozone-free oxygen (Table 3). Only 78–89% of the ¹⁴C was captured in the KOH traps providing additional evidence for the direct volatilization of aniline. Analysis of base solutions also indicated the formation of volatile ozonation products from trifluralin columns treated with ozone, as ¹⁴CO₂ accounted for only 72–83% of the total observed activity in the traps. In contrast, trifluralin concentrations and activities remained largely unchanged in the ozone-free oxygen treated columns after 4 min. Loss due to volatilization was minimal after 30 min of exposure, with less than 6% reduction in initial concentrations. Total activity in base

Table 3

Percent contaminant and activity remaining after exposure to ozone gas and ozone-free oxygen

Soil	Ozone			Ozone-free oxygen		
	Aniline/activity (4 min)	Trifluralin/activity (4 min)	Trifluralin/activity (30 min)	Aniline/activity (4 min)	Trifluralin/activity (4 min)	Trifluralin/activity (30 min)
Evesboro C1	2/45	37/93	3/70	74/73	99/101	94/93
Evesboro B2	3/71	46/96	6/76	78/77	98/99	94/96
Christiana Ap	23/83	75/95	30/85	89/96	101/103	97/101

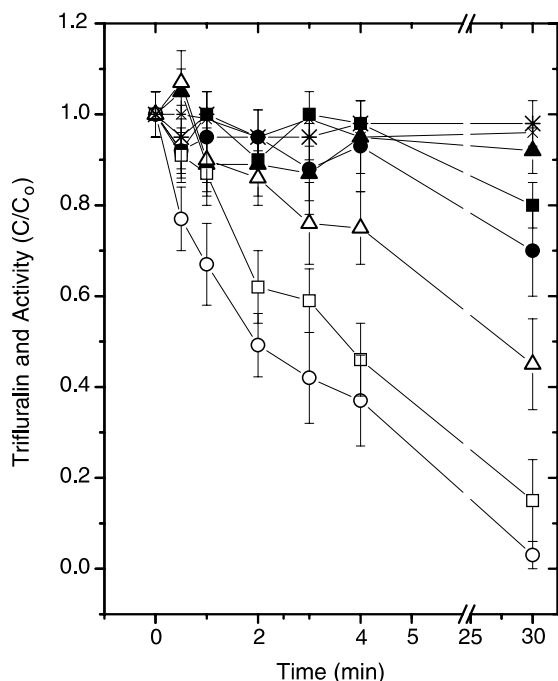


Fig. 4. Treatment of trifluralin in soil columns using ozone gas: (○) parent compound remaining in Evesboro C1 soil columns; (●) ^{14}C remaining in Evesboro C1 soil columns; (□) parent compound remaining in Evesboro B2 soil columns; (■) ^{14}C remaining in Evesboro B2 soil columns; (△) parent compound remaining in Christiana soil columns; (▲) ^{14}C remaining in Evesboro B2 soil columns. (×) and (*) represent the parent and ^{14}C remaining using ozone-free oxygen.

solutions accounted for greater than 90% of the activity lost from soil columns (data not shown).

Contaminant and ^{14}C loss rates were slower for trifluralin amended soil columns (Fig. 4), which required ≈ 30 min to achieve removals comparable to aniline. This is expected due to a lower ozone reaction rate of trifluralin, as aniline is among the most highly reactive with ozone; $k = 10^6 \text{ l/M}\cdot\text{s}$ in aqueous systems (Hoigne and Bader, 1983). Contaminant removal rates for aniline and trifluralin were slower in Christiana soil columns,

suggesting competitive ozone consumption from soil organic matter.

Total ^{14}C decreased less rapidly than parent material in soil columns. The residual activity present was due to intermediate ozonation products. GC/MS analysis indicated that nitrobenzene and nitrosobenzene were present in the extract from aniline amended soil columns. This direct oxidation of the aromatic amine group is in agreement with studies performed by Chan and Larson (1991) on ozone reactions with aniline in aqueous systems. However, other aqueous phase aniline condensation reaction products, such as benzidine and azobenzene, reported by these authors, were not identified in our experiments. Further oxidation of the aniline oxidation products was indicated by the loss of total activity in the soil.

GC/MS analysis of extract of trifluralin-amended soils exposed to ozone revealed the presence of 2,6-dinitro-4-(trifluoromethyl) aniline, 2,6-dinitro-*N*-propyl-4-(trifluoromethyl) benzamine, and 2,6-dinitro-*N*-propyl-*N*-acetyl-4-(trifluoromethyl) benzamine in trifluralin columns (Fig. 5). These products were not observed in extract of columns treated with ozone-free oxygen. Oxidation of the propyl groups to form 2,6-dinitro-*N*-propyl-*N*-acetyl-4-(trifluoromethyl) benzamine, or the loss of one or both of the propyl groups, to form 2,6-dinitro-*N*-propyl-4-(trifluoromethyl) benzamine aniline and 2,6-dinitro-4-(trifluoromethyl) aniline may result in increased volatility. This is suggested by the low proportion of $^{14}\text{CO}_2$ activity in the base solutions in the traps.

3.3. Factors influencing contaminant removal

Improved solubility due to decreased hydrophobicity is expected by the cleavage of the trifluralin aromatic ring and removal of the propyl groups. Both of these reactions should facilitate contaminant removal from soils. Experiments were performed to examine the effect of ozone on contaminant removal. Loss of trifluralin from soil columns treated with ozone-rich water and ozone-free water is shown in Fig. 6. A significant increase in removal rate was observed in Evesboro soil columns eluted with ozone-rich versus ozone-free water. Similar

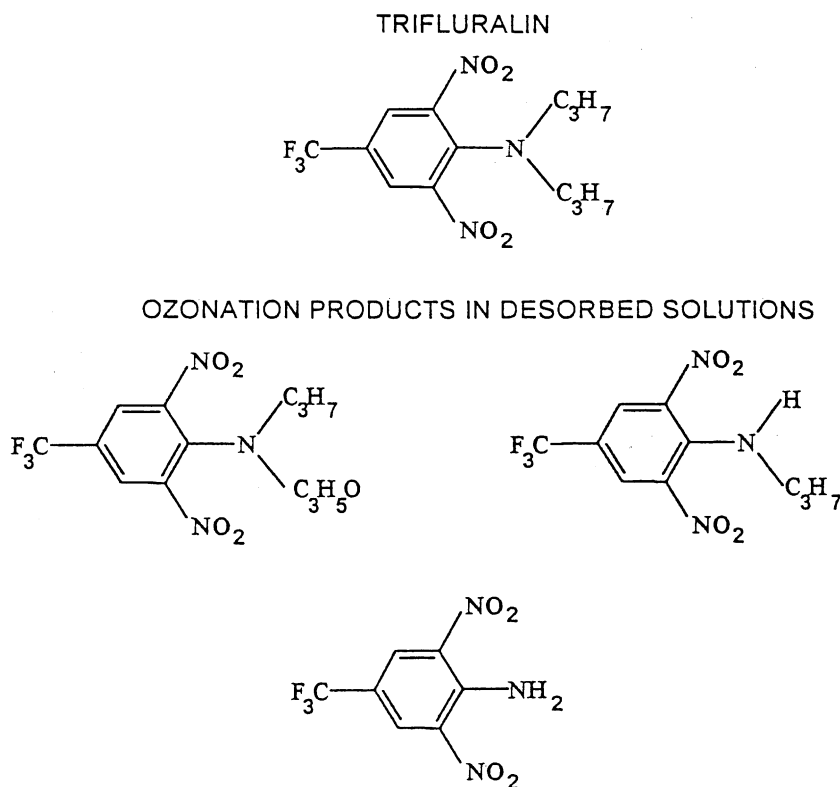


Fig. 5. Structures of trifluralin and reaction products.

experiments were conducted using aniline amended soil columns (Fig. 7). Only a slight increase was observed in all three soils. This suggests that ozone is more effective in enhancing the removal of highly insoluble contaminants.

Aniline has a solubility of 40 mg/l as compared to a solubility of 0.3 mg/l for trifluralin. The increased removal rate for trifluralin can be due to a dual effect. First, ozone reacts with trifluralin affording a more hydrophilic, thus more water soluble and more mobile, compounds. Furthermore, ozone could also react with the soil organic matter forming more hydrophilic sorbent with a decreased sorption capacity (Torrents et al., 1997). To distinguish between these two processes, experiments were conducted using soils amended with pentachloroaniline or hexachlorobenzene. Pentachloroaniline and hexachlorobenzene are essentially unreactive with ozone, thus any increase in contaminant removal rate would be the result of changes in the sorption properties of the soil organic matter. Ozone was found to have no effect on pentachloroaniline or hexachlorobenzene loss rates. Furthermore, the DOC was measured in the soil eluent. No differences were observed in the DOC concentrations of the eluent using ozone-rich or ozone-free water.

Additional evidence of ozone reacting with trifluralin was found in the GC/MS of the ethyl acetate extract of the soil eluent. Complete cleavage of *N*-propyl groups was observed by the detection of 2,6-dinitro-4-(trifluoromethyl) aniline (m/z 251 (base), 235, 148). *N*-propyl oxidation was indicated by the formation of a higher molecular weight compound (m/z 349 (base), 319, 275, 246) which can correspond to 2,6-dinitro-*N*-propyl-*N*-acetyl-4-(trifluoromethyl) benzamine or 2,6-dinitro-*N*-propyl-*N*-propanal-4-(trifluoromethyl) benzamine, (standards were not available). Several other products were also observed with base peaks of 293, 275 and 273.

To further examine the effect of organic matter, lignin was added to Evesboro C1 columns to achieve organic matter contents of 0.15% and 0.35%. The soils were then amended with trifluralin and treated with ozone-rich water or ozone free water. The results show that the addition of lignin significantly reduces removal rates in either the ozone-rich or ozone-free eluted columns (Fig. 8). Similar results were observed for the aniline amended soil columns. These results suggest that an increase in organic matter content significantly decreases the effectiveness of ozone-rich water to enhance desorption.

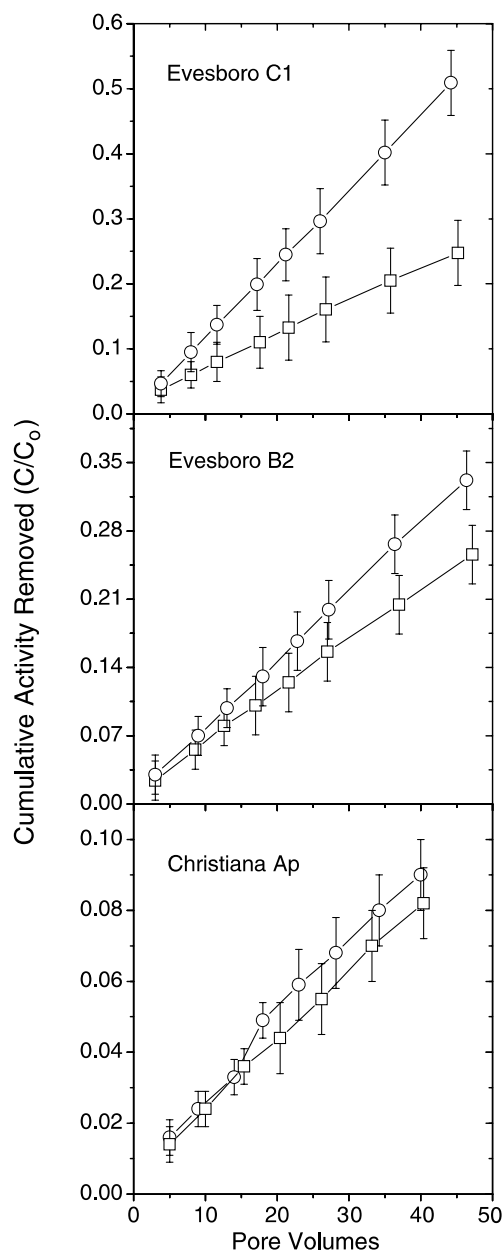


Fig. 6. Removal curves for soil columns amended with trifluralin: (○) ozone-rich water; (□) ozone-free water.

Soil pore water pH may also influence contaminant removal efficiency in soil systems treated with ozone-rich water. Hydroxide is known to react with ozone to form highly reactive free radicals, including hydroxyl radical. In aqueous systems, free radicals may react with organic constituents, or they may react with free radical scavengers, such as carbonate. The effect of hydroxide and

ozonation efficiency is dependent on soil conditions and contaminant reactivity.

Column studies were performed to determine the effect of pH on contaminant removal. In the studies, removal rates increased with decreased pH for soil amended with trifluralin and exposed to ozone-rich water buffered at pH 4, 7, and 12 (Fig. 9). This effect was not observed when ozone-free water buffered at the same pH levels was used suggesting that the decreased removal at high pH may be due to loss of reactive species by free-radical scavenging, slow reactivity of free radicals with trifluralin, or product influences. The hydroxyl radical is expected to react by hydroxylation of trifluralin, while ozone may result in carbon bond cleavage or significant oxidation. Hydroxylation may not provide the necessary hydrophilic character to improve removal.

The removal from aniline-amended columns was rapid and not affected by pH. Thus, while removal of aniline was too fast to be measurably influenced by ozone or pH, both affected trifluralin removal. It is important to note that when pesticides, and other chemicals, are in contact with the soil for long periods of time, the pollutants become more deeply adsorbed and thus less available. The results reported here are for soils freshly amended with pesticide. One should expect that the aging process would diminish the capabilities of ozone to desorb and oxidized sorbed chemicals.

4. Conclusions

Ozone gas effectively degraded aniline and trifluralin in soil columns, suggesting that it can be used as a treatment method for soils contaminated with some agrochemicals. Competing reactions with soil organic matter reduced contaminant removal rates. The ozone gas consumed ranged from 0.028 to 1.82 mg O₃/g soil for the soils studied. During treatment, the ozone demand exerted by soil organic matter may be significant. For the Christiana soil, this may amount to over 1.8 kg of O₃ per ton of soil. Thus, an ozone generator capable of producing 4.5 kg O₃ per hour would require over 9 h to meet the soil organic matter ozone demand.

Ozone-rich water increased the removal rate of trifluralin from soil columns, indicating a potential for application of ozone to chemically enhance soil washing processes. However, the use of ozone-rich water to improve contaminant removal would appear to have limited potential use, as even low soil organic carbon, i.e., 0.07–0.15%, can effectively consume dissolved ozone. Similarly, soil pore water pH may also reduce treatment efficiency. Removal rates for trifluralin substantially decreased with increased pH, suggesting free radical scavenging, reduced reaction rate, or low product solubility.

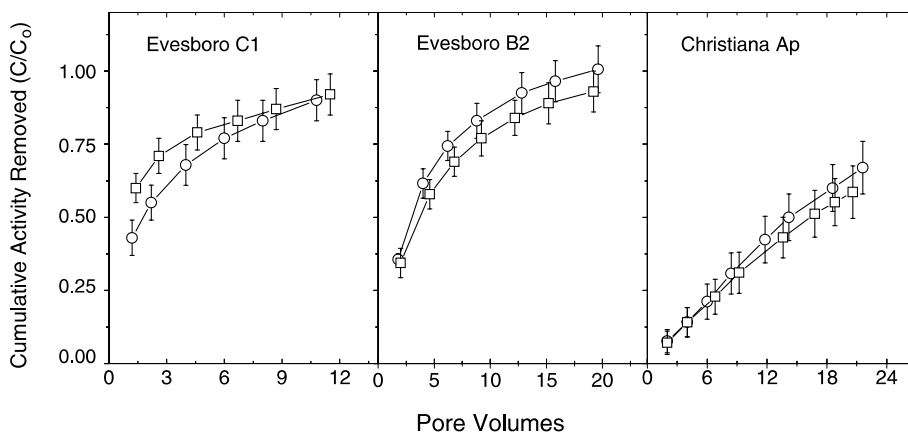


Fig. 7. Removal curves for soil columns amended with aniline: (○) ozone-rich water; (□) ozone-free water.

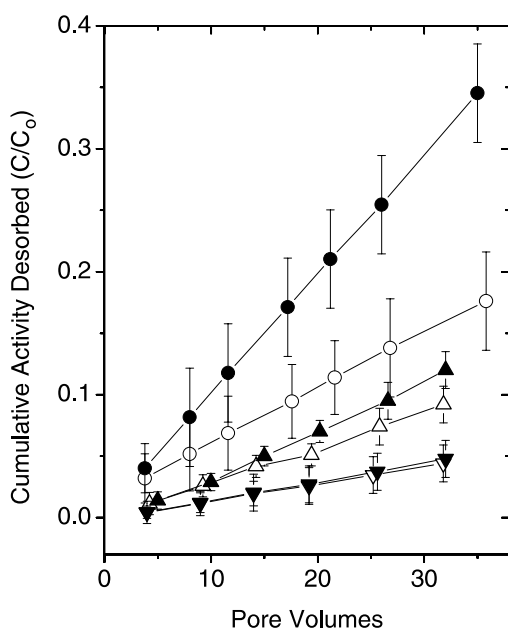


Fig. 8. Effect of lignin on removal: (a) ozone-rich water, closed symbols; (b) ozone-free water, open symbols; (○) 0.0% OM; (Δ) 0.15% OM; (◇) 0.35% OM.

While the use of ozone would not be practical for wide-spread, low-level contamination, it may be practical for localized areas with significant pesticide contamination, such as spill sites. Further studies need to address the effect of aging. Field studies are necessary to further assess the benefits and limitations of the use of ozone gas and ozone-rich water for remediation of pesticide contaminated sites.

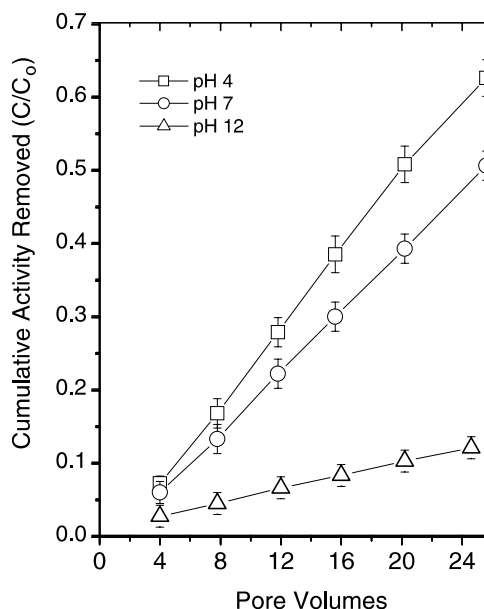


Fig. 9. Effect of pH on the removal of trifluralin from Evesboro C1 soil columns.

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